

# A New Copper(II)–Iron(II) Complex [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] based on Nitroprusside: Synthesis, Structure and Spectroscopic Studies

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A new complex [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] (acac<sup>−</sup> = acetylacetonate, py = pyridine, bpy = 2,2′-bipyridine) has been prepared and investigated by single-crystal X-ray analysis, IR (infrared), EPR (electron paramagnetic resonance) and Mössbauer spectroscopy, and variable-temperature magnetic susceptibility. The structure consists of two [Cu(acac)(bpy)(py)]<sup>+</sup> cations and one [Fe(CN)<sub>5</sub>(NO)]<sup>2−</sup> anion. It crystallizes in space group *P*1 with cell parameters *a* = 9.963(3), *b* = 10.485(2), *c* = 11.749(2) Å, *α* = 111.35(2), *β* = 96.18(2), *γ* = 95.43(2)°. The structure refined to a final *R*-value of 0.045 for 2103 observed reflections [*I* ≥ 3σ(*I*)]. The copper(II) atoms are in a distorted square-based pyramidal geometry with two oxygen atoms of the acac<sup>−</sup> ligand and two nitrogen atoms of the bpy ligand lying in the basal plane and one nitrogen atom of py occupied in the apical position. Mössbauer and magnetic susceptibility studies evidence the low-spin state of the iron(II) metal center. EPR spectroscopy and magnetism show the operation of weak magnetic interactions in the solid state, which may be transmitted through the π-stacking interactions between the bpy ligands of adjacent [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] constitutive units.

The study of pentacyanonitrosylmetallate hydrates of transition metal elements is of current interest.<sup>1</sup> complexes of this class have been employed as molecular sieves, cation exchangers, electron scavengers and most recently as radionuclide sorbents.<sup>2,3</sup> The nitroprussides are also currently used as reversible inhibitors of superoxide dismutases.<sup>4</sup> Recently, cyano-bridged compounds based on the nitroprusside ion have been reported which exhibit weak antiferromagnetic interactions between the paramagnetic metal ions through the Fe(CN)<sub>5</sub>(NO)<sup>2−</sup> complex diamagnetic anions.<sup>5–7</sup> In this context, we prepared a new complex [Cu(bpy)][Fe(CN)<sub>5</sub>(NO)] · 2H<sub>2</sub>O (bpy = 2,2′-bipyridine), and unfortunately recrystallization of the complex gave rise to another complex [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] (acac<sup>−</sup> = acetylacetonate, py = pyridine). Here we report the synthesis, single-crystal X-ray analysis and IR (infrared), EPR (electron paramagnetic resonance), magnetic and

Mössbauer studies of the novel compound, [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)].

## Experimental

Elemental C, H, N analyses were carried out with a Perkin–Elmer analyzer model 240. IR spectra was recorded on a Nicolet 5DX FT-IR spectrophotometer in the 4000–400 cm<sup>−1</sup> range. Samples were run as KBr pellets. The room-temperature EPR powder spectrum was recorded at X-band with a JES-FE1XG EPR spectrometer using Mn as a reference, and the room-temperature and 110 K DMF (*N,N*-dimethylformamide) solution spectra were recorded at X-band with a Bruker ESR ER 200D-SRC spectrometer. Variable-temperature magnetic susceptibility data were obtained as previously described<sup>8</sup> on a powdered sample with a Quantum Design MPMS SQUID susceptometer. Diamagnetic corrections were applied by using Pascal's constants. Mössbauer measurements were obtained on a constant-acceleration

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conventional spectrometer with a 25-mCi source of <sup>57</sup>Co (Rh matrix). Isomer shift values ( $\delta$ ) throughout the paper are given with respect to metallic iron at room temperature. The absorber was a sample of 120 mg of microcrystalline powder enclosed in a 2 cm diameter cylindrical plastic sample holder, the size of which had been determined to optimize the absorption. Variable-temperature spectra were obtained in the 293–4.2 K range, by using an MD 306 Oxford cryostat, the thermal scanning being monitored by an Oxford ITC4 servocontrol device ( $\pm 0.1$  K accuracy). A least-squares computer program<sup>9</sup> was used to fit the Mössbauer parameters and determine their standard deviations of statistical origin (given in parentheses).

[Cu(bpy)][Fe(CN)<sub>5</sub>(NO)]·2H<sub>2</sub>O (**1**). To a solution of [Cu(bpy)](NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O<sup>10</sup> (1 mmol) in water (10 mL) was added dropwise an aqueous solution of Na<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)]·2H<sub>2</sub>O (1 mmol) with stirring at room temperature. A light blue precipitate was deposited rapidly. The mixture was stirred for ca. 20 min, and the precipitate produced was collected by suction filtration, thoroughly washed with water and dried in the air. Yield: almost quantitative. Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>8</sub>O<sub>2</sub>CuFe: C, 38.19; H, 2.56; N, 23.76%. Found: C, 38.62; H, 2.72; N, 23.26%. IR (cm<sup>-1</sup>):  $\nu_{(C\equiv N)}$  2200, 2150;  $\nu_{(N=O)}$  1950.

[Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] (**2**). Solid [Cu(bpy)][Fe(CN)<sub>5</sub>(NO)]·2H<sub>2</sub>O (0.5 mmol) was dissolved in a hot acetylacetone and pyridine mixture (ca. 1:2 v/v, 20 mL) to give a green solution. Blue crystals suitable for X-ray analysis formed in the resulting solution within a few hours. Yield: 30%. Anal. Calcd. for C<sub>45</sub>H<sub>40</sub>N<sub>12</sub>O<sub>5</sub>FeCu<sub>2</sub>: C, 53.42; H, 3.98; N, 16.61. Found: C, 53.42; H, 4.10; N, 16.38. IR (KBr: cm<sup>-1</sup>):  $\nu_{(C\equiv N)}$  2140(s) and 2070(w);  $\nu_{(N=O)}$  1880(vs);  $\nu_{(C-O)}$  1577(s) and 1520(s). M.p. > 180 °C (decomp.).

*Crystal structure determinations of 2.* The unit-cell parameters were calculated from the setting angles of 25 reflections using the least-squares technique. Intensities were collected using an Enraf-Nonius CAD-4 diffractometer in the  $\omega$ -2 $\theta$  scan mode using Mo-K $\alpha$  radiation. Three standard reflections monitored every 60 min showed no intensity variation during the data collection. An empirical absorption correction was made.<sup>11</sup> The structure was solved by direct methods using Siemens SHELXTL-PC program and refined by the full-matrix least-squares method.<sup>12</sup> Of the 2808 independent reflections, 2103 reflections were considered observed [ $I \geq 3\sigma(I)$ ] and used in the refinement. Atomic scattering factors were taken from Ref. 13. The final  $R$  and  $wR$  values were minimized by  $R = \sum(|F_o| - |F_c|) / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_c)^2]^{1/2}$ , where  $w = 1/[\sigma^2(F)]$ . Fractional atomic coordinates for **2** are listed in Table 1.

Crystal data, C<sub>45</sub>H<sub>40</sub>Cu<sub>2</sub>FeN<sub>12</sub>O<sub>5</sub>: 299 ± 1 K, space group  $P\bar{1}$ , crystal dimensions 0.10 × 250 × 35 mm, triclinic,  $a = 9.963(3)$ ,  $b = 10.485(2)$ ,  $c = 11.749(2)$  Å,

Table 1. Atomic coordinates and  $U_{eq}$  (in Å<sup>2</sup> × 10<sup>3</sup>).

Atom	x	y	z	$U_{eq}$
Cu(1)	0.0790(1)	0.2829(1)	0.3448(1)	44(1)
O(1)	-0.0918(5)	0.1625(5)	0.2963(4)	56(2)
O(2)	0.0950(5)	0.2677(5)	0.1796(4)	55(2)
C(4)	-0.2933(8)	0.0271(9)	0.1745(8)	80(4)
C(5)	-0.1618(8)	0.1140(8)	0.1892(7)	56(3)
C(6)	-0.1168(9)	0.1349(8)	0.0880(7)	66(4)
C(7)	0.0019(8)	0.2078(7)	0.0868(6)	51(3)
C(8)	0.0348(10)	0.2209(9)	-0.0315(6)	75(4)
N(11)	0.0562(5)	0.3455(6)	0.5228(5)	42(2)
C(12)	-0.0350(7)	0.2854(8)	0.5690(7)	52(3)
C(13)	-0.0414(8)	0.3327(9)	0.6939(7)	60(4)
C(14)	0.0477(9)	0.4424(9)	0.7702(7)	61(4)
C(15)	0.1460(8)	0.5067(8)	0.7256(6)	51(3)
C(16)	0.1462(7)	0.4540(7)	0.5986(6)	39(3)
C(17)	0.2438(6)	0.5111(7)	0.5385(6)	41(3)
C(18)	0.3419(7)	0.6220(7)	0.5993(7)	50(3)
C(19)	0.4297(8)	0.6665(8)	0.5317(8)	64(4)
C(20)	0.4117(8)	0.5991(8)	0.4058(8)	60(4)
C(21)	0.3106(7)	0.4889(8)	0.3506(7)	53(3)
N(22)	0.2256(5)	0.4457(5)	0.4146(5)	41(2)
N(31)	0.2183(6)	0.1253(6)	0.3451(5)	47(2)
C(31)	0.2418(8)	0.0805(8)	0.4362(8)	63(4)
C(32)	0.3228(9)	-0.0188(10)	0.4317(9)	79(5)
C(33)	0.3805(9)	-0.0767(9)	0.3277(11)	84(5)
C(34)	0.3576(9)	-0.0337(9)	0.2332(8)	72(4)
C(35)	0.2791(8)	0.0689(8)	0.2460(7)	60(4)
Fe(1)	1/2	1/2	0	58(1)
C(1)	0.4904(8)	0.3601(8)	0.0682(6)	51(3)
N(1)	0.4874(8)	0.2769(8)	0.1082(6)	76(4)
C(2)	0.4066(7)	0.3661(8)	-0.1537(7)	48(3)
N(2)	0.3539(7)	0.2845(7)	-0.2452(6)	64(3)
Nc <sup>a</sup>	0.3359(7)	0.5447(7)	0.0471(6)	44(3)
On <sup>b</sup>	0.2350(7)	0.5751(7)	0.0765(6)	66(3)

<sup>a</sup>Nc = 1/2 N + 1/2 C. <sup>b</sup>On = 1/2 O + 1/2 N.

$\alpha = 111.35(2)$ ,  $\beta = 96.18(2)$ ,  $\gamma = 95.43(2)^\circ$ ,  $V = 1125(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho(\text{calcd}) = 1.497$  g cm<sup>-3</sup>,  $\rho(\text{measured}) = 1.48(2)$  g cm<sup>-3</sup> (by flotation),  $\mu = 1.351$  mm<sup>-1</sup>,  $F(000) = 518$ ,  $\theta_{\text{max}} \leq 23^\circ$ ,  $R_{\text{int}} = 0.042$ ,  $R = 0.045$ ,  $R_w = 0.050$ ,  $S = 1.38$ .

## Results and discussion

*Syntheses.* Reaction of coordinately unsaturated Cu(bpy)<sup>2+</sup> with Fe(CN)<sub>5</sub>(NO)<sup>2-</sup> in an aqueous solution gives the mixed metal complex [Cu(bpy)][Fe(CN)<sub>5</sub>(NO)]·2H<sub>2</sub>O. The shift to higher wavelength of  $\nu_{(C\equiv N)}$  suggests the formation of cyanide bridges with respect to that of the free nitroprusside.

Since complex **1** hardly dissolves most common organic solvents, we tried to recrystallize it from a Hacac-py mixture; this did not give single crystals of **1**, but unexpectedly gave **2** instead.

*Crystal structure of 2.* The structure is ionic and consists of two [Cu(acac)(bpy)(py)]<sup>+</sup> cations and one [Fe(CN)<sub>5</sub>(NO)]<sup>2-</sup> anion as shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2.

The two copper atoms are symmetry-related. Based

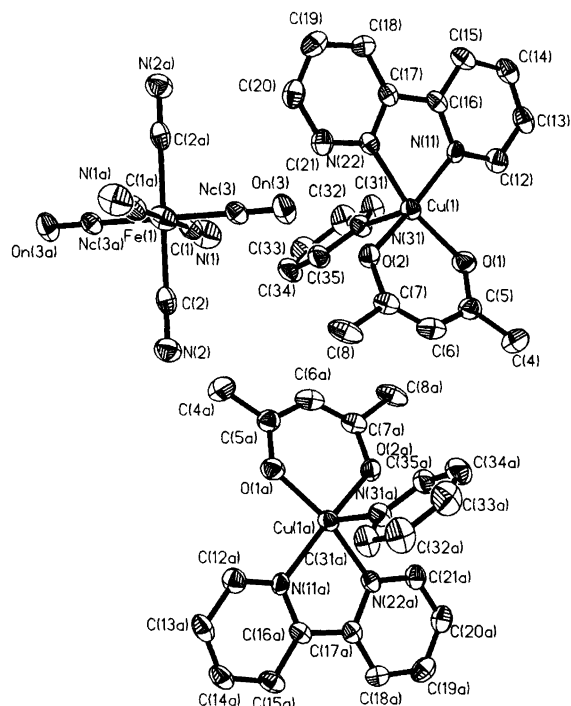


Fig. 1. An ORTEP drawing (30% probability ellipsoids) of  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$  showing the atomic labeling scheme. Symmetry code:  $a^*1-x, 1-y, -z$ .

Table 2. Selected bond distances (in Å) and angles (in  $^\circ$ ).<sup>a</sup>

Cu–O(1)	1.916(5)	Cu–O(2)	1.913(5)
Cu–N	1.997(6)– 1.993(5)	Cu(1)–N(31)	2.257(7)
Fe(1)–Nc(3)	1.830(7)	Nc(3)–On(3)	1.135(10)
O(1)–C(5)	1.267(9)	O(2)–C(7)	1.271(8)
N=C	1.132(13)– 1.135(8)	C(5)–C(6)	1.396(13)
C(6)–C(7)	1.350(12)		
O(1)–Cu(1)–O(2)	93.8(2)	O(1)–Cu(1)–N(11)	91.3(2)
O(1)–Cu(1)–N(22)	164.9(2)	O(1)–Cu(1)–N(31)	178.1(7)– 178.6(7)
O(1)–Cu(1)–N(31)	98.4(2)	O(2)–Cu(1)–N(11)	166.2(2)
Fe(1)–Nc(3)–On(3)	178.6(7)	O(2)–Cu(1)–N(22)	91.4(2)
O(2)–Cu(1)–N(31)	94.7(2)	N(11)–Cu(1)–N(22)	80.6(1)
N(11)–Cu(1)–N(31)	97.2(2)	N(22)–Cu(1)–N(31)	95.3(2)
C(1)–Fe(1)–Nc(3)	89.9(4)	Nc(3)–Fe(1)–Nc(3) <sup>b</sup>	180.0(1)

<sup>a</sup>On = 1/2 O + 1/2 N, Nc = 1/2 N + 1/2 C. <sup>b</sup>Symmetry code:  $1-x, 1-y, -z$ .

on the bond angles and lengths, the coordination polyhedron around each copper ion may be regarded as a square pyramid. The basal coordination plane is occupied by the N(11) and N(22) atoms of one bpy ligand, and the O(1) and O(2) atoms of one acac<sup>−</sup> ligand. The apical position is occupied by the N(31) atom of the py ligand with a Cu–N distance of 2.257(7) Å. The largest deviation from the least-squares plane through N(11)N(22)O(1)O(2) is 0.01 Å at N(11) and N(22), and the copper atom lies 0.22 Å out of this plane towards the apical N(31) atom. With an average value of

1.995(5) Å, the Cu–N in-plane distances are close to each other, and in good agreement with those previously reported for Cu–bpy complexes.<sup>14,15</sup> The Cu–O bond lengths average 1.914(5) Å, which is in the usual range for copper(II). The  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  complex ion has an axially compressed octahedral geometry. Based on the physical measurements and the equilibrium of charge, NO<sup>+</sup> is present in the compound, and the presence of other anions such as  $\text{Fe}(\text{CN})_6^{4-}$  is unlikely. The iron is located at the crystallographic inversion center, and the ligands around the iron(II) ion in the *trans* positions are symmetry-related. Consequently the NO and the CN groups *trans* to each other cannot be distinguished from each other and are statistically disordered onto both axial coordination sites. Figure 2 shows the  $\pi$ -stacking between bpy ligands of adjacent trinuclear  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$  constitutive units. The interplanar separation for the stacked bpy ligands is about 3.45 Å. No other intermolecular contacts have been evidenced which could account for the observed crystal packing. The nearest C $\cdots$ Cu and Cu $\cdots$ Fe distances are 5.198 and 6.911 Å, respectively.

**Spectroscopic and magnetic properties for 2.** The most interesting feature in the infrared spectrum of  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$  is the low wavenumber characterizing the NO vibration compared to other nitroprusside salts. The  $\nu_{\text{NO}}$  values for compounds including nitroprusside range from 1880 to 1940  $\text{cm}^{-1}$ .<sup>16–18</sup> It is known that the polar NO group is sensitive to the electric field generated by its environment.<sup>18</sup> Consequently, the low 1880  $\text{cm}^{-1}$  value observed indicates that the electrons of the NO group are attracted more towards the oxygen atom, which is probably due

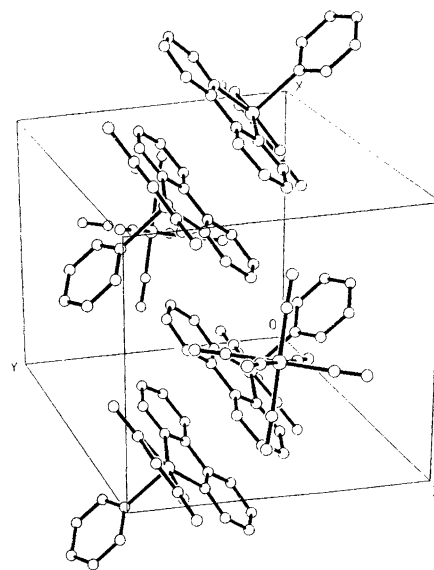


Fig. 2. The unit cell of  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$  showing the nature of the  $\pi$ -stacking between the neighboring coordinated bpy molecules.

to the high field generated by the [Cu(acac)(bpy)(py)]<sup>+</sup> cations. A similar observation has been made in the case of the alkaline salts of nitroprusside: substitution of K<sup>+</sup> for Cs<sup>+</sup> cations results in a downward shift of  $\nu_{\text{NO}}$ .

The X-band EPR powder spectrum of [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] at room temperature shows a broad and anisotropic signal (Fig. 3a), the analysis of which affords  $g_{\parallel}=2.19$  and  $g_{\perp}=2.06$ . The

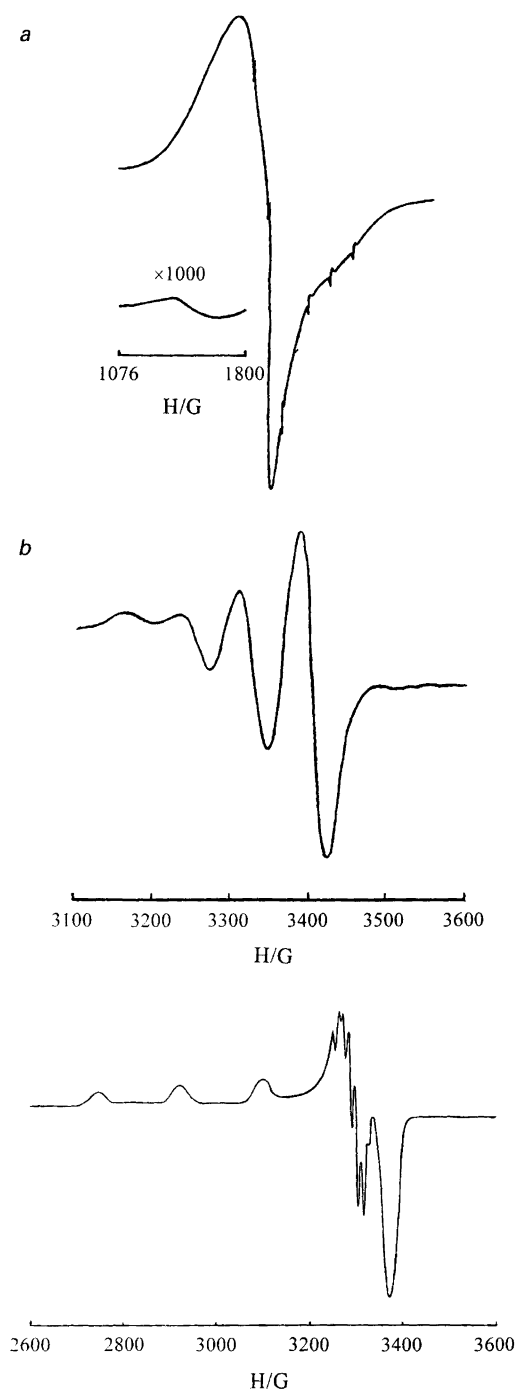


Fig. 3. X-Band ESR spectra of [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)]: (a) powder at room temperature; (b) top: in DMF at room temperature; bottom: frozen DMF at 110 K.

trend,  $g_{\parallel} > g_{\perp} > g_e = 2.0023$ , indicates that the unpaired electron is located in the  $d_{x^2-y^2}$  orbital.<sup>19</sup> The  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$  ratio provides information about the exchange interaction between copper centers in the polycrystalline state. For the compound under study, the  $G \approx 3.17$  value suggests the presence of a spin-spin interaction.<sup>20</sup> Actually, a half-field transition is observed at  $g = 4.25$ , suggesting the existence of magnetic interactions between adjacent copper(II) ions. The absence of any other absorption in the EPR spectrum is consistent with the low-spin state of iron(II) in [Fe(CN)<sub>5</sub>(NO)]<sup>2-</sup>. The solution and frozen solution EPR spectra (Figs. 3b and 3c, respectively) also indicate a  $d_{x^2-y^2}$  ground state based on the above-mentioned criterion. However, there is no half-field signal in the solution spectra, which probably results from cancellation of the weak magnetic interactions due to the removal of the intermolecular  $\pi$ -stacking interactions responsible for the crystal packing. This observation is in agreement with the ionic structure evidenced by single-crystal X-ray diffraction for this compound. Analysis of the hyperfine structure of the frozen solution spectrum affords  $g_{\parallel} = 2.32$  and  $A_{\parallel} = 193 \times 10^{-4} \text{ cm}^{-1}$  (178 G) parameters typical of mononuclear copper compounds. Based on  $g_{\text{av}}$  (2.12) and  $A_{\text{av}}$  ( $72 \times 10^{-4} \text{ cm}^{-1}$ , 73 G) parameters calculated from the room-temperature solution spectrum,  $g_{\perp}$  (2.02) and  $A_{\perp}$  ( $19.3 \times 10^{-4} \text{ cm}^{-1}$ , 20.5 G) parameters may be evaluated, which are in good agreement with those reported for mononuclear copper compounds.

The Mössbauer spectra of [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] recorded at 293, 80 and 4.3 K consist of a single quadrupole split doublet. They were least-squares fitted with Lorentzian curves, and the resulting isomer shift [ $\delta = -0.206(1)$  (80 K),  $-0.195(1)$  (4.3 K)] and quadrupole splitting parameters [ $\Delta E_Q = 1.887(2)$  (293 K), 1.913(1) (80 K), 1.928(2) (4.3 K)] clearly indicate the presence of low-spin iron(II). These parameters are similar to those of other nitroprussides.<sup>6,21,22</sup> The isomer shift values are weakly temperature-dependent owing to second-order Doppler shift, and the relatively large  $\Delta E_Q$  values for low-spin iron(II) are consistent with the significant departure of the ligand field from cubic symmetry, which results from the mixed CN/NO ligands to the iron (see structural section).<sup>23</sup>

The  $\chi_m T$  value per [Cu(acac)(bpy)(py)]<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)] (Fig. 4) at 300 K is equal to  $0.91 \text{ cm}^3 \text{ K mol}^{-1}$ , close to that expected for two non-interacting copper(II) ions ( $0.98 \text{ cm}^3 \text{ K mol}^{-1}$ ), thus confirming the low-spin state of iron(II) in this compound. There is almost no temperature dependence of  $\chi_m T$ , except for a small lowering at temperatures lower than 8 K yielding a minimal  $\chi_m T$  value of ca.  $0.64 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K, which may be due to either minute magnetic interactions between the nearest copper(II) ions or a zero field splitting (ZFS) of the coupling state. This conclusion is in agreement with the results of the X-ray structural determination, leading to the description of this compound as a cationic and anionic species with large

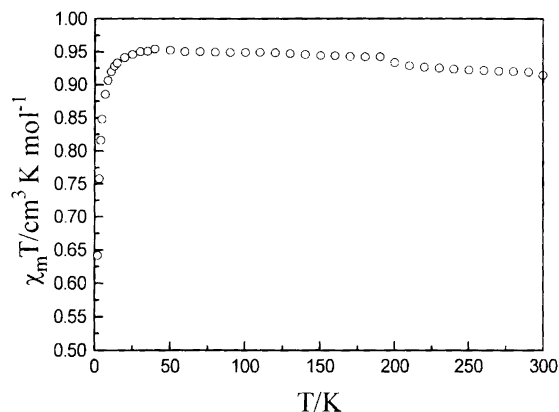


Fig. 4. The plot of  $\chi_M T$  versus temperature for  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$ .

Cu...Cu distances but  $\pi$ -stacking interactions between bpy ligands of adjacent  $\text{Cu}(\text{acac})(\text{bpy})(\text{py})^+$  constitutive units. These  $\pi$ -stacking interactions probably mediate very weak magnetic interactions<sup>24</sup> in the solid state as suggested by EPR spectroscopy.

In summary, a new copper(II)-iron(II) compound  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$ , have been prepared and characterized by single-crystal X-ray diffraction, spectroscopic and magnetic studies. The reported compound can be considered as a variation of sodium nitroprusside in which  $\text{Na}^+$  is substituted for the  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]^+$  complex cation. EPR and magnetic studies on  $[\text{Cu}(\text{acac})(\text{bpy})(\text{py})]_2[\text{Fe}(\text{CN})_5(\text{NO})]$  indicate that weak magnetic interactions operate in the solid state between adjacent copper(II) ions ( $\text{Cu}\cdots\text{Cu} = 5.198 \text{ \AA}$ ), while the crystal packing suggests that  $\pi$ -stacking contacts between their coordinated bpy ligands may transmit these weak magnetic interactions.

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